

Oxygenates in Vermont Gasoline and Groundwater

VTDEC/WMD Study Using
USEPA/OUST Funding
Fall 2002-Spring 2006

Outline

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- Statistical Analysis (Phase II)
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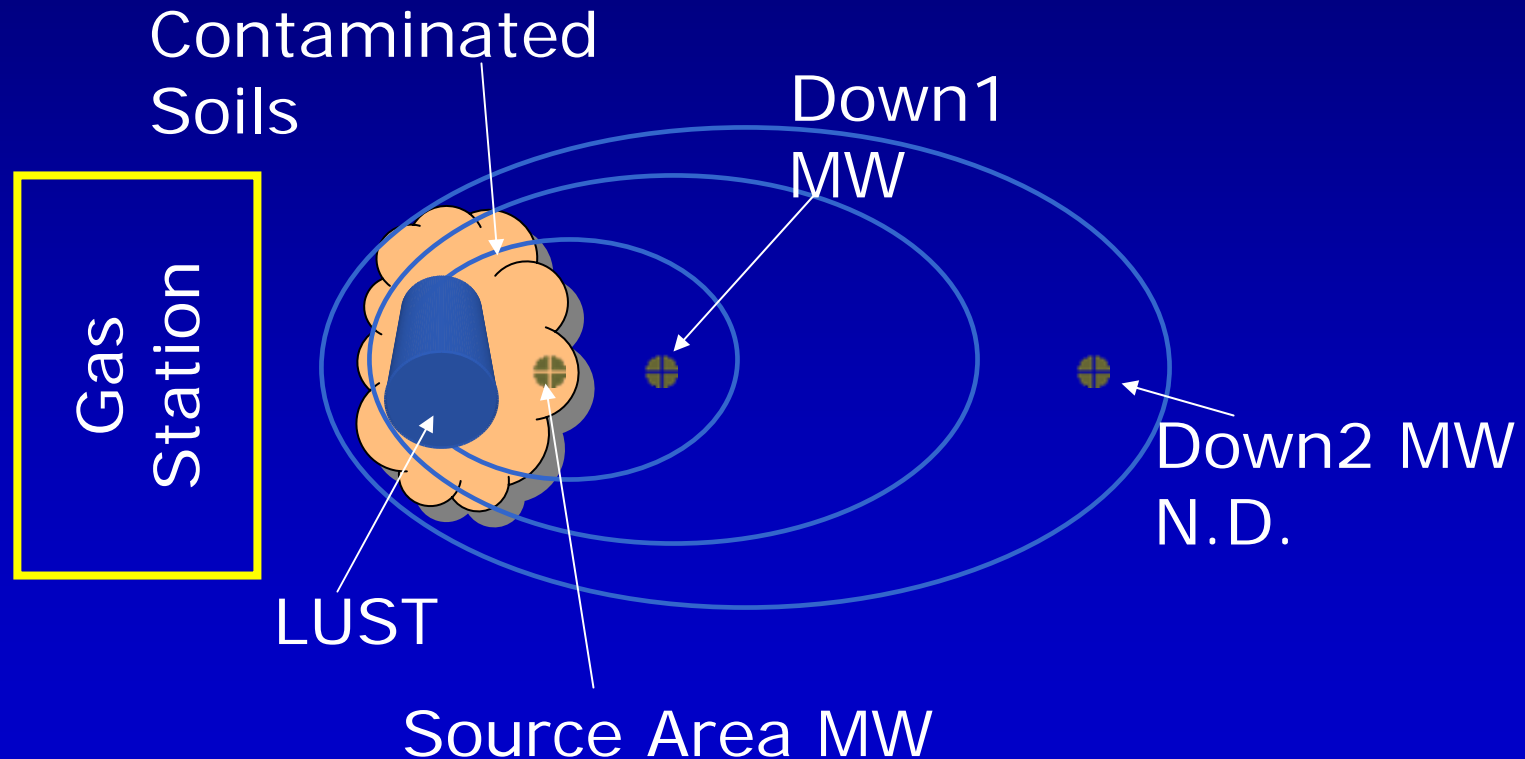
Objectives of Study – PHASE I

- To determine oxygenate concentrations in different grades of fuels (regular, mid-grade, and super).
- To determine oxygenate concentrations in groundwater at LUST sites.
 - Transit down the plume axis
 - In source area wells
 - In highly contaminated wells outside of the source area
 - In contaminated wells near the leading edge of the plume

Objectives of Study – PHASE II

- To compare approaches of different EPA analytical methodologies for fuel oxygenates in groundwater at several wells for numerous sites
- To determine if current COC list (MTBE) is appropriate
 - Or, if other ethers and TBA should be analyzed at all petroleum sites

Wells Being Sampled



Methodology (Product)

- DEC staff to obtain product samples from various stations around the state.
- Samples taken during summer & winter periods to determine variations in product composition.
- Approximately 60 stations sampled (240 samples)

Methodology (Product)

- Samples analyzed in tenths of a percent for:

Ethanol	ETBE	Benzene
Methanol	TAME	Aromatics
TBA	DIPE	Olefins
MTBE	O ₂	Saturates

- Lab uses GS360 fuel analyzer



Lab Set-Up

Methodology (GW)

- Consultants obtains samples from MWs selected by DEC project managers during routine sampling events
- Samples sent to DEC lab
- Approximately 60 stations (180 samples)
- Samples analyzed with a detection limit in $\mu\text{g/L}$

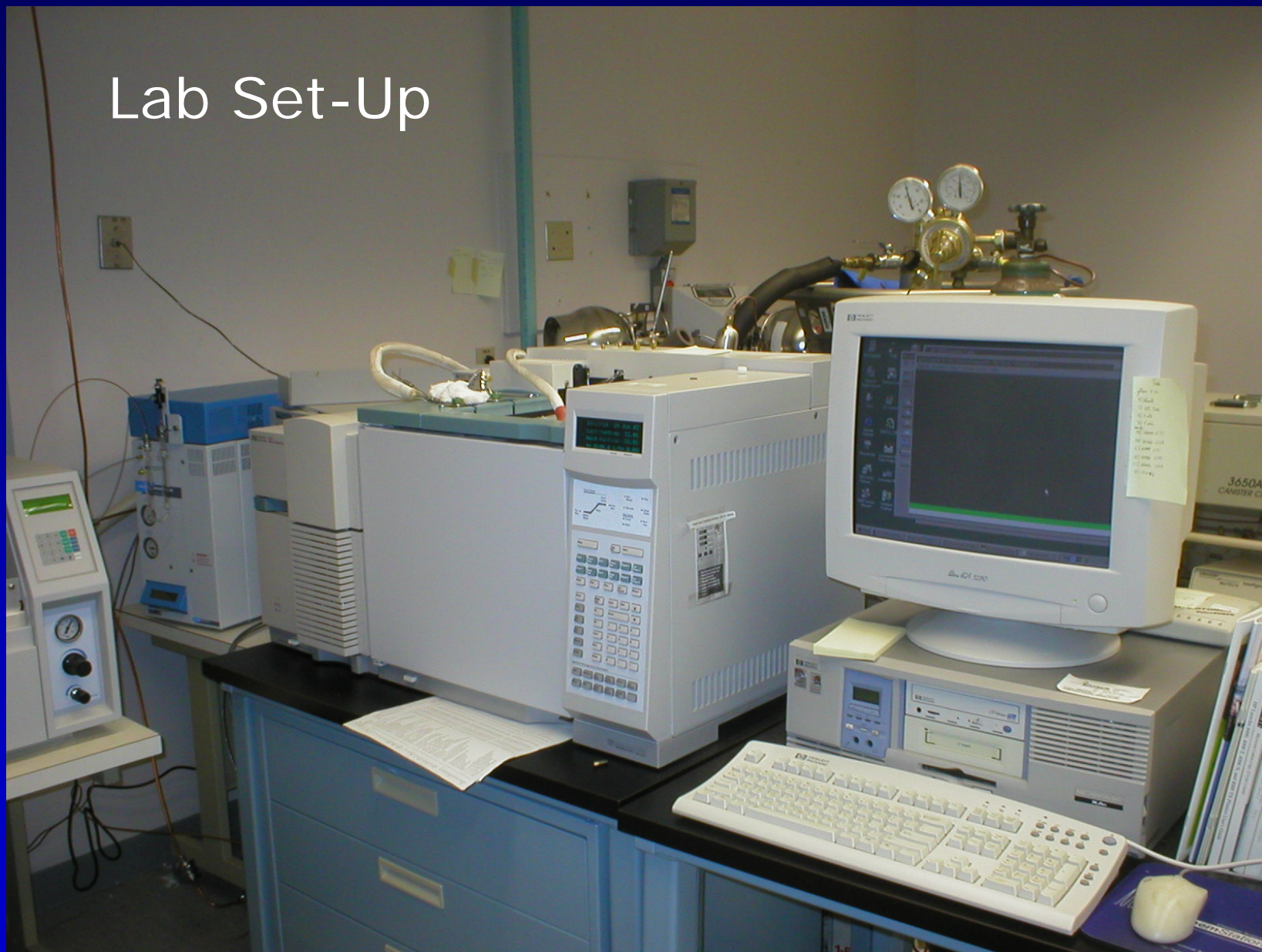
Methodology (GW)

- Samples analyzed for:

MTBE	BTEX
TBA	TMBs
ETBA	Naphthalene
DIPE	TAME

- Samples analyzed with GC/MS by EPA Method 8260

Lab Set-Up



Fuel Sample Results (PHASE I)

	MTBE	TBA	Ethanol	Methanol
Mean	2.3 %	0.3 %	0.05 %	0.2 %
Min	0.05 %	0.05 %	0.05 %	0.05 %
Max	12.9 %	0.6 %	0.05 %	0.4 %

	ETBE	TAME	DIPE	O ₂	Benzene
Mean	0.1 %	1.4 %	0.05 %	0.8 %	1.0 %
Min	0.05 %	0.05 %	0.05 %	0.16 %	0.5 %
Max	0.4 %	5.0 %	0.05 %	2.35 %	1.5 %

- Oxygenates higher in summer months than winter months
- Oxygenates higher in super than regular

Groundwater Results – PHASE I

	Source	Down 1	Down 2
MTBE	345,000 ⁶	93,100 ⁶	519 ⁶
TBA	811 ³	811 ³	ND
ETBE	622 ⁷	240 ⁷	1 ²
DIPE	296 ⁴	26 ⁸	2 ²
TAME	20,300 ⁷	15,500 ⁶	999 ¹
Benzene	31,100 ⁴	4800 ⁵	800 ⁴
BTEX	133,000 ¹	15,000 ⁵	3000 ⁴

- Maximum concentration measured in µg/L
- X¹ – Superscript indicates site identifier

Statistical Analysis – PHASE I

- Contracted with University of Vermont (UVM) to perform statistical analysis
- Data on previous slides the preliminary evaluation only
- Follow-up data evaluation not yet conducted

Phase II Work

- All MWs sampled during 2002 & early 2003 were re-sampled in 2004
- Three samples per MW, two preserved with HCl, one with TSP
 - One sample analyzed utilizing “normal” protocol (20°C, GC/MS)
 - Remaining two samples heated to 80°C (following EPA recommendations)

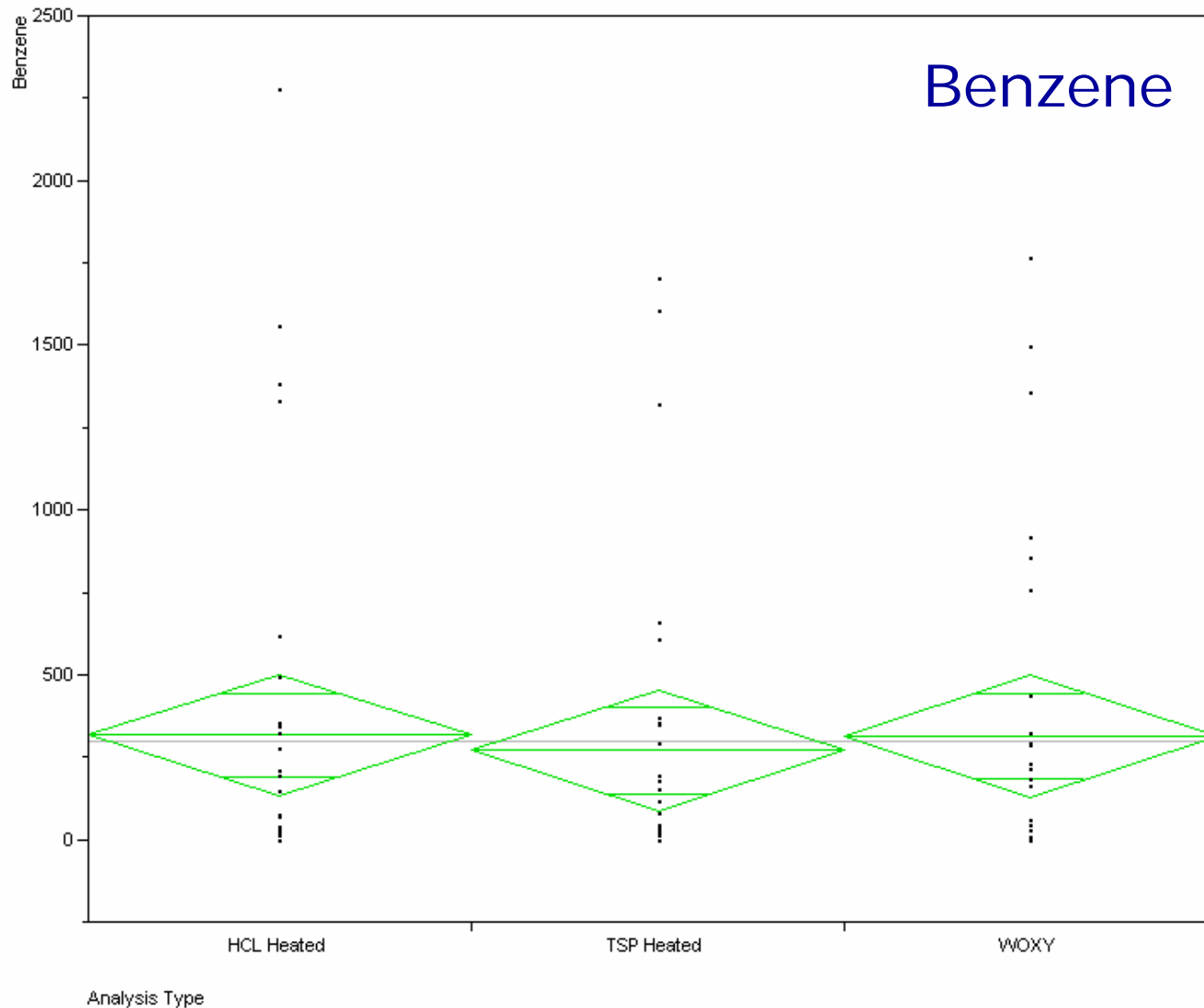
Theory of Testing

- Samples analyzed at 20°C w/HCl preservative (WOXY method) won't reveal alcohols -namely TBA- at low detection limits.
- Samples heated to 80°C and preserved with HCl (HCl heated method) will reveal low levels of TBA, but also lower levels of ethers, due to hydrolysis.
- To prevent these issues, EPA has recommended preserving samples with a base and heating samples to 80°C (TSP heated method), to drive out alcohols and eliminate hydrolysis.

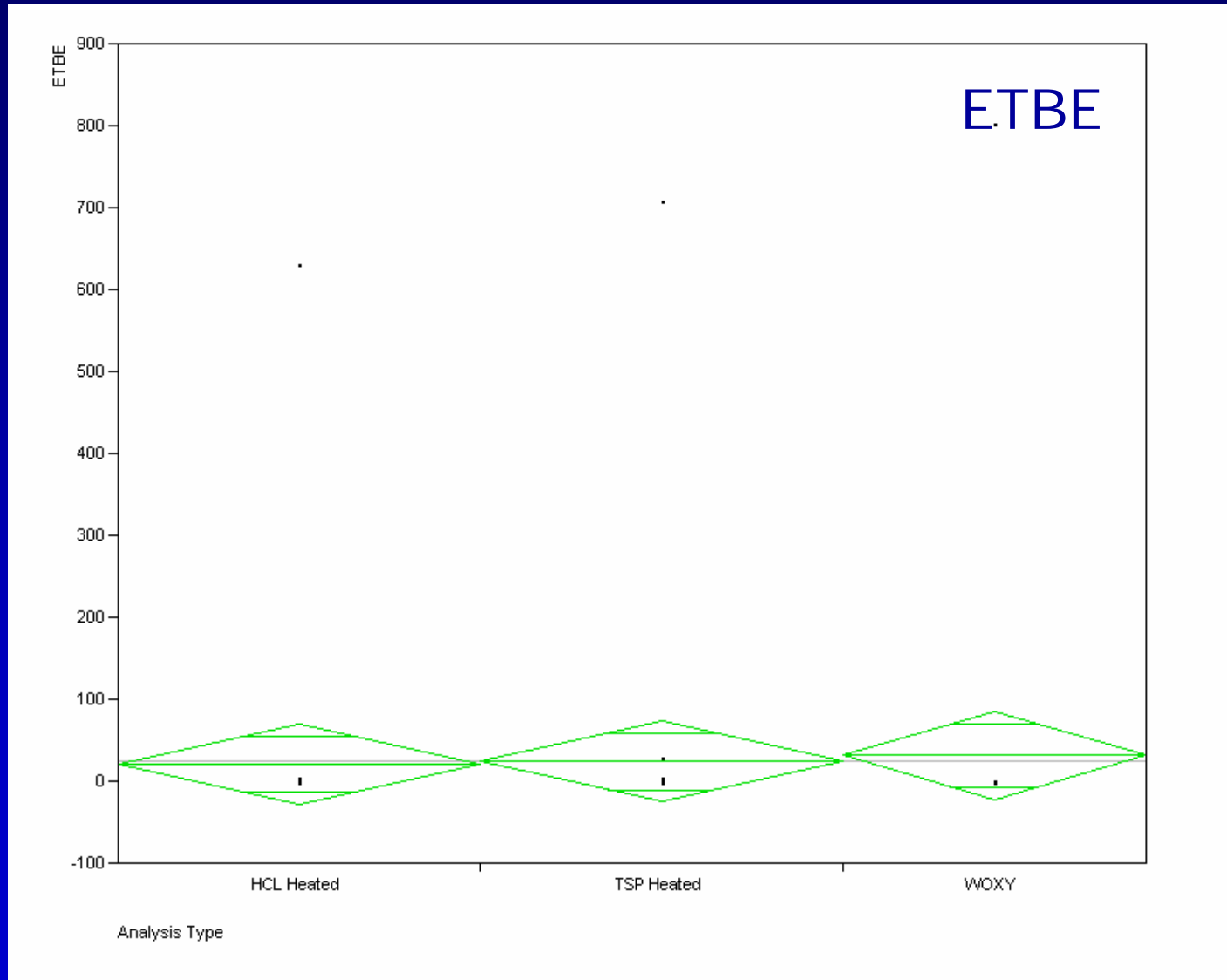
Statistical Analysis – PHASE II

- Data has been hand-groomed
 - Some data still questionable, though unlikely to significantly alter the results
- Data for each analytical method (WOXY, HCl Heated, and TSP Heated) entered into JMP to conduct one-way analyses of variance (ANOVA)

ANOVA – Sample Results



ANOVA – Sample Results



ETBE ANOVA Results

Summary of Fit

Rsquare	0.001071
Adj Rsquare	-0.02329
Root Mean Square Error	134.6854
Mean of Response	25.81941
Observations (or Sum Wgts)	85

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Analysis Type	2	1595.2	797.6	0.0440	0.9570
Error	82	1487493.3	18140.2		
C. Total	84	1489088.4			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
HCL Heated	30	21.4593	24.590	-27.46	70.377
TSP Heated	30	24.9090	24.590	-24.01	73.827
WOXY	25	32.1440	26.937	-21.44	85.730

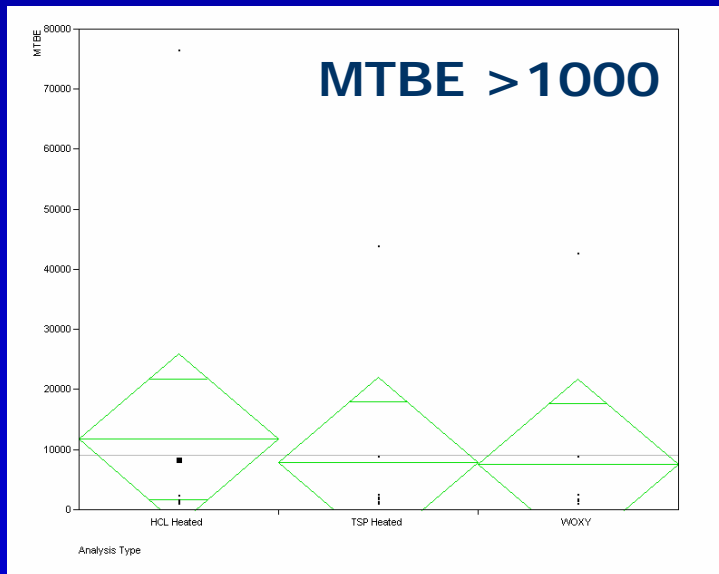
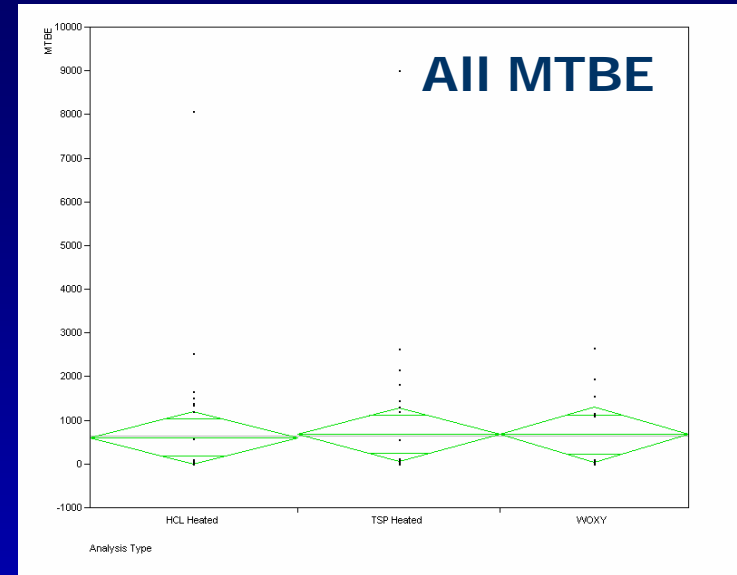
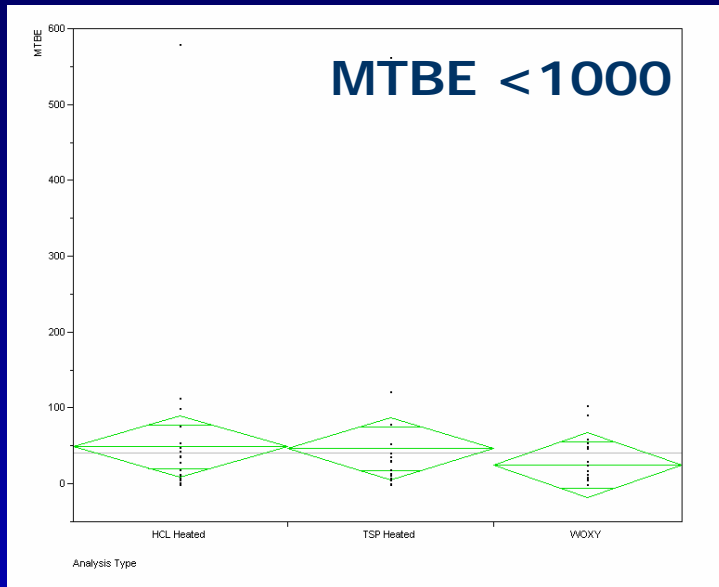
Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]- Mean[j]	WOXY	TSP Heated	HCL Heated
WOXY	0.000	7.235	10.685
TSP Heated	-7.235	0.000	3.450
HCL Heated	-10.685	-3.450	0.000

Alpha = 0.05

ANOVA – Sample Results



- MTBE samples split into two groups (<1000 µg/L and >1000 µg/L) for ANOVA
- Also conducted an ANOVA on all MTBE samples
- Determined that there is no statistical difference between the methodologies at high and low concentrations

ANOVA - Data

	Mean			F Ratio	Prob > F
Constituent	HCI Heated	TSP Heated	WOXY		
Benzene*	318.78	273.13	316.26	0.0766	0.9263
DIPE	1.51	1.46	0.00	1.0854	0.3425
ETBE*	21.46	24.91	32.14	0.0440	0.9570
MTBE*	611.16	689.89	682.43	0.0203	0.9800
TAME	343.72	247.55	280.56	0.0627	0.9393
TBA*	66.88	70.28	84.62	0.0549	0.9466

* Data has been groomed to remove gross outliers

Results

- ANOVA results dictate that there is no statistical difference between any of the three analytical methods
- One caveat: at low concentrations, the standard approach may miss some ethers or TBA
 - Data indicates this may occur in approximately 10% of the samples (3 out of 32)

Laboratory Data – PHASE II

Site Number	Site Name	Well	Analysis Type	Benzene	DIPE	ETBE	MTBE	TAME	TBA
921256	Georgia Mobil	OW-3	WOXY		0	0		0	DL 5000
			HCl Heated	31.72	0	0	1.67	80.39	37.54
			TSP Heated	35.1	0	0	0.53	0	15.34
941597	Fleming Texaco	FT-3	WOXY	0	0	0	0	0	DL 2000
			HCl Heated	0	0	0	0	0	157.75
			TSP Heated	0	0	0	0	0	127.26
992581	Derby Line Mainway	MW-4	WOXY	5	0	0	0		100 DL 200
			HCl Heated	43.48	0	0	0	0.58	90.93
			TSP Heated	48.89	0	0	0	0.63	136.35

Conclusions

- Even in a non-RFG state, there are high levels of oxygenates in the fuel and in GW
- At high concentrations, the type of analytical method utilized does not appear to matter
- At low concentrations, samples should be preserved with TSP and heated to 80°C
- Should look at all ethers and TBA, perhaps other alcohols as well

Next Steps

- Work with lab to clean up the data
- Compile all data into one dataset
- Compare (with JMP) all constituents with each other at varying concentration ranges
- Evaluate effects of remediation and MNA-only sites in source and two downgradient wells
- Evaluate inorganics for relation to COC levels in each of the MWs